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(54) [Title of the Invention] Electrode Separator for Electrochemical Device

(57) [Abstract]
[Structure] An electrode separator for an electrochemical device, comprising laminated porous films wherein polyolefin resin porous film layers (A) with a melting point of at least 160°C and a polyolefin resin porous film layer (B) with a melting point of between 100 and 150°C are laminated into an A/B/A three-layered structure, said layer B serving as the intermediate layer having a thickness of at least 3 µm, and the laminated porous films as a whole having a thickness of between 10 and 30 µm.

[Effects] A low melting point layer is used as the intermediate layer, and it has greater thickness, and thus greater volume, resulting in better shut down function in the event of excess current.

[Claims]

[Claim 1] An electrode separator for an electrochemical device, comprising laminated porous films wherein polyolefin resin porous film layers (A) with a melting point of at least 160°C and a polyolefin resin porous film layer (B) with a melting point of between 100 and 150°C are laminated into an A/B/A three-layered structure (where the two A layers may be the same or different), said layer B serving as the intermediate layer having a thickness of at least 3 µm, and the laminated porous films as a whole having a thickness of between 10 and 30 µm.

[Claim 2] A separator as defined in Claim 1, wherein the polyolefin resin constituting the layers A has a melting point of at least 200°C.

[Claim 3] A separator as defined in Claim 1 or 2, wherein layer B is between 5 and 20 µm thick.

[Claim 4] A separator as defined in any of Claims 1 through 3, wherein the laminated porous films have a mean porosity of between 30 and 65%.

[Claim 5] A separator as defined in any of Claims 1 through 4, wherein the laminated porous films have a mean pore diameter of between 0.01 and 5 µm.

[Claim 6] A separator as defined in any of Claims 1 through 5, wherein the polyolefin resin constituting the layers A is polypropylene or poly (4-methylpentene-1).

[Claim 7] A separator as defined in any of Claims 1 through 6, wherein the polyolefin resin constituting layer B is polyethylene, an ethylene-propylene copolymer, or poly (butene-1).

[0001]

[Background of the Invention]

[Field of Industrial Application]

The present invention relates to a separator that is interposed between electrodes in an electrochemical device, and in particular to an electrode separator for an electrochemical device which is intended to cope with electrode shorts or the uncontrollable heat (referred to as thermal runaway) resulting from such shorts.

[0002]

Electrochemical devices with electrodes, particularly battery cells, have a structure in which at least a pair of electrodes face each other, with an electrolyte interposed between the electrodes. A narrower distance between electrodes is desirable to

make a more compact cell. When the distance between the electrodes is narrowed, a separator consisting of a porous sheet is commonly interposed between the electrodes in order to prevent them from coming into contact with each other and to ensure the absorption of electrolyte.

[0003]

In light of the foregoing, and because of their excellence as battery cells, lithium cells are typical of electrochemical devices with a narrow distance between electrodes.

[0004]

The positive electrode, separator, and negative electrode are wound when manufacturing electrochemical devices with a narrow distance between electrodes, particularly lithium cells or lithium ion cells, resulting in pressure between the electrodes as well as between electrode and separator, while the separator is also subject to tensile force.

[0005]

The electrode surface is not necessarily smooth, but is on the contrary inherently uneven and is coated with carbon beads. When the separator interposed between the electrodes has low strength, the unevenness of an electrode can press into the separator, sometimes coming into contact with the other electrode, with the potential for so-called internal shorts. The cell is also exposed to the possibility of external shorts.

[0006]

In either case, shorts result in the flow of substantial short current in the cell, causing overheating in the cell. This overheating in the cell leads to the possibility of explosions from gas resulting from the volatilization and (or) decomposition of the nonaqueous electrolyte used as the cell electrolyte. Since the gas that is produced is flammable, not only is there the inherent danger of it escaping out of the cell through explosion, but the danger is even greater when the negative electrode active material is a highly active light metal such as in lithium cells.

[0007]

[Prior Art]

A separator consisting of a laminate of a high melting point polyolefin porous film A and a low melting point polyolefin porous film B has been proposed in Japanese Laid-Open Patent Application 2-77108) in view of the above. This prior invention is understood to have been proposed in an effort to remedy the drawbacks of porous polyolefin monolayer films known at that time.

[0008]

That is, according to this proposal, when a short occurs, resulting in excessive current in the cell, the relatively low melting point polyolefin porous film layer is melted by the heat produced at that time and automatically clogs the pores formed by the short, allowing the separator to lower the likelihood of a total breakdown. That is, the separator

in this proposal can be said to have a shut down function (shut down function refers to the phenomenon where excess current flows in the cell as a result of internal and external shorts, leading to an increase in the cell temperature from the ensuing Joule heat, so that at least one layer constituting the separator melts, and the molten material fills the micropores, serving as an insulator which not only affords electrical insulation but also prevents ion migration and prevents the flow of current).

[0009]

The two layers with differing melting points preferably form an A/B or B/A/B (A: high melting point; B: low melting point) layered structure.

[0010]

This prior invention can be said to offer its own solution. However, the inventors of the present invention have learned that the desired layer structure given above is not satisfactory.

[0011]

That is, with an A/B or B/A/B layered structure, the heat generated during shorts results in considerable destruction of the low melting point layer, that is, the layer B, and the laminate ends up consisting of nothing but the high melting point layer, that is the layer A, in some parts, tending to result in the problem of a high incidence of shorts, which is typical of porous polyolefin monolayered separators. In the case of external shorts, the layer B is temporarily clogged and sealed by the heat produced during the short, but since the layer B is in a molten state, minute conductive materials which can occur on the electrodes protrude into the layer B, making it highly possible that portions will consist of essentially nothing but the layer A. Excess current in the portions consisting of nothing but the layer A can result in even higher cell temperatures, with more pronounced problems typical of monolayered structures.

[0012]

Another problem is the tendency for laminated sheets to curl in A/B structures which are asymmetrical in the thicknesswise direction, posing practical problems since this hinders processing during the manufacture of cells and the like.

[0013]

A similar separator has also been disclosed in Japanese Patent Publication 4-38101.

[Means Used to Solve the Above-Mentioned Problems]

[0014]

[Summary of the Invention]

An object of the present invention is to remedy the aforementioned drawbacks, primarily by providing a separator consisting of porous polyolefin resin film layers with a specific layered structure.

[0015]

[Essence of the Invention]

That is, the electrode separator for an electrochemical device in the present invention is characterized by comprising laminated porous films wherein polyolefin resin porous film layers (A) with a melting point of at least 160°C and a polyolefin resin porous film layer (B) with a melting point of between 100 and 150°C are laminated into an A/B/A three-layered structure (where the two A layers may be the same or different), said layer B serving as the intermediate layer having a thickness of at least 3 µm, and the laminated porous films as a whole having a thickness of between 10 and 30 µm.

[0016]

[Effects of the Invention]

The separator of the present invention consists of a laminate of polyolefin resin porous films, where a low melting point layer (layer B) is interposed between high melting point layers (layers A), thereby resolving the drawbacks of conventional separators in which the desired layer structure had the low melting point layer on the electrode side. In addition to the specified triple-layered structure, the laminate of the present invention is also characterized in that the low melting point interlayer is relatively thick. This thickness means that the low melting point interlayer has a relatively large resin volume. Following the sharp decrease in volume when the interlayer melts, the molten material between the two high melting point porous film layers is pressed by these two layers, resulting in more uniform melt fluidity between the two high melting point porous film layers, and allowing better shut down function to be maintained up to higher temperatures than with conventional separators.

[0017]

[Detailed Description of the Invention]

[Laminated Structure]

General Description

The laminated porous films for the separator in the present invention form a laminated structure having an A/B/A structure, in which the low melting point polyolefin resin film layer (layer B) is interposed between two high melting point polyolefin resin film layers (layers A). The two layers A are both porous polyolefin resins with a melting point of at least 160°C, but as long as they meet this definition, the two layers may be the same or different in terms of the type of polyolefin resin used, the melting point, and (or) the mean porosity and mean pore diameter. Here, "high melting point" means a melting point of at least 160°C, and "low melting point" means a melting point of between 100 and 150°C.

[0018]

The low melting point layer serving as the interlayer is a relatively thick 5 µm or more. The laminated porous films as a whole are 10 to 30 µm thick. A desirable specific

example of such laminated porous films has a porosity of between 30 and 65%, and a mean pore diameter of 0.01 to 5 μm .

[0019]

The A/B/A laminated structure may be formed with the layers joined at various points, but it is preferable for each layer to be essentially joined together over the entire surface.

[0020] High Melting Point Polyolefin Resin Film Layer (Layer A)

The polyolefin resin film layer constituting layer A consists of a polyolefin resin with a melting point of at least 160°C, and preferably at least 200°C, such as between about 220 and 250°C. When the melting point is lower than 160°C, not only does the separator tend to be completely destroyed during shorts, but an adequate difference in melting point from the low melting point layer B cannot be preserved, resulting in an inadequate shut down function. "Melting point" is the endothermic peak temperature that is measured when 10 mg sample is heated at a rate of 10°C/min from room temperature in a nitrogen stream using a differential scanning calorimeter (DSC 30, by Mettler).

[0021]

Examples of "polyolefin resins" in the present invention include α -olefins, particularly C₂ to C₆ homopolymers, copolymers thereof, copolymers consisting primarily of such an α -olefin, such as copolymers containing at least 50 mol% of an α -olefin and another copolymerizable ethylenic unsaturated monomer, as well as blends consisting primarily of these, such as a content of 50 wt% or more, and other resins.

[0022]

In film manufacturing techniques, such polyolefin resins are usually not cross-linked, but the polyolefin resin may be cross-linked if it can be made into a film or it can undergo cross-linking treatment following the manufacture of the film. The polyolefin resin may be drawn or treated within an acceptable range by a method relating to the molecular orientation, crystallization, or the like as appropriate for polymers or resin materials. The polyolefin resin in the present invention may also be blended with organic or inorganic fillers, thermal stabilizers, antioxidants, lubricants, antistatic agents or other such additives, as is commonly done with polymers and resin materials.

[0023]

The polyolefin resin of layer A is distinguished from that of the low melting point layer B in that the melting point is at least 160°C.

[0024]

Polyolefin resins meeting these melting point conditions are well known, and one with the desired melting point may be selected. Desirable examples of the polyolefin resin for layer A include polypropylene, poly (4-methylpentene-1), and

poly (3-methylbutene-1). Of these, polypropylene and poly (4-methylpentene-1) are preferred, while poly (4-methylpentene-1) is particularly preferred.

[0025]

The polyolefin resin film for layer A is commonly 3 to 20 μm , and preferably 5 to 15 μm , so as to be thick enough to allow the laminated structure to be readily made but to avoid a laminated structure that is too thick, and to lower the possibility of shorts.

[0026]

The layer A is a porous film. The following description on the manufacture of laminates is provided as reference for the manufacture of the film and its porosification.

[0027] Low Melting Point Polyolefin Resin Film Layer (Layer B)

Layer B is essentially the same as layer A except that it has a lower melting point than layer A and is at least 5 μm thick.

[0028]

That is, the polyolefin resin for layer B has a melting point of between 100 and 150°C, and preferably between 110 and 135°C. A melting point lower than 100°C results in the danger of the shut down function being triggered during normal operations, whereas one higher than 150°C is less safe because a longer time is taken until the shut down function is activated during shorts.

[0029]

Such low melting point polyolefin resins are well known. Specific examples include polyethylene, ethylene-propylene copolymers, and poly (butene-1). Of these, polyethylene and poly (butene-1) are preferred, while poly (butene-1) is even more preferred. These can be mixed with another resin such as polypropylene, provided that the shut down function is not thereby compromised.

[0030]

The difference in melting point from layer A should be at least 30°C, preferably at least 50°C, and even more preferably at least 80°C, to ensure adequate separator applications, such as good shut down function.

[0031]

As noted above, a feature of the present invention is that the layer B serving as the interlayer is at least 3 μm thick. The layer B (and A) preferably has a porosity of 30 to 65%, and specifically is often around 50%. Because of the pronounced decrease in volume when it melts from the heat produced during shorts, the layer B in the present invention is made thicker, with a commensurate increase in the volume of the layer B resin, so as to compensate for such pronounced decreases in volume.

[0032]

A lithium cell was manufactured to examine the thickness of the layer B, revealing that the layer B should be at least 3 μm , preferably at least 5 μm , and even more preferably between 7 and 15 μm , thick.

[0033] Formation and Porosification of Laminate Structure

The laminate structure can typically be formed by coextrusion or extrusion lamination, except when there is a particular desire to join pre-fabricated films. Of these, coextrusion is preferred.

[0034]

The coextrusion and extrusion lamination of thermoplastic resins are well known techniques. Any method meeting this objective can be used upon taking into consideration the resin melting point and differences in melting points called for in the present invention as well as other polymer properties.

[0035]

It has already been noted above that the laminated structure can be stretched or treated by other methods relating to the molecular orientation, crystallization or the like, whatever the method used to manufacture the laminate.

[0036]

The laminated structure thus created is not porous except when porous films are first made and then joined.

[0037]

The nonporous film can be rendered porous by any method meeting this objective.

[0038]

One method is to make a polyolefin nonporous film using a microdispersion of heterogeneous solids such as inorganic fine powders, and to then provide strain such as that involved in drawing to bring about interfacial breakdown between the heterogeneous solids, thereby producing holes and making the material porous. However, it is difficult to control the dispersion of the heterogeneous solids in this method, and the pore size distribution tends to be rather broad.

[0039]

Another generally desirable method for rendering nonporous films porous is to make a nonporous film using a dispersion of a solvent-soluble material, followed by treatment with a solvent to extract the solvent-soluble material.

[0040]

The solvent-soluble material used in such cases is an organic liquid or solid, an organic or inorganic powder, or the like which can be dispersed in the desired polyolefin resin.

[0041]

Typical examples of organic liquids or solids include compounds that are known as plasticizers, such as phthalic acid diesters, aliphatic dibasic acid esters, phosphate triesters, glycol esters, and epoxy compounds. Typical examples of phthalic acid esters include dibutyl, di-n-octyl, di(2-ethylhexyl), dinonyl, dilauryl and other esters. Di-n-octyl phthalate (DOP) is one of the more desirable ones.

[0042]

When it comes to organic and inorganic powders, organic powders can be considered more desirable since it is intended for a porous film being used in an electrochemical device. Water-soluble organic powders such as saccharide powders are specific examples.

[0043]

A nonporous film obtained by kneading and dispersing such a soluble material in the polyolefin resin is treated with a solvent suited to the soluble material in question so as to elute the soluble material. When the soluble material is a phthalic acid diester or phosphate triester given as examples above, examples of solvents include halocarbons (such as trichloromethane and trichloroethane), ketones (such as acetone and methyl ethyl ketone), lower carboxylic acid esters (such as ethyl acetate), lower alkanols (such as methanol and isopropyl alcohol, and aromatic hydrocarbons (such as toluene and xylene).

[0044]

To ensure that the pores obtained following the elution of the soluble material produce the desired porosity and pore diameter, the amount blended and the kneading conditions are selected in light of the solubility parameters between the soluble material and the selected polyolefin resin when the soluble material is a liquid or solid, while the amount of powder that is blended and the particle size are selected when the soluble material is a powder. These can vary between layers. Tears can be produced around the powder when the material is stretched because the solvent readily penetrates when the soluble material is a powder.

[0045]

When the polyolefin resin is poly (butene-1) and poly (4-methylpentene-1), the intended DOP dispersion state can be obtained by blending 40 to 150 phr DOP and by kneading the materials for 1 to 30 minutes at 200 to 280°C. The polyolefin resin can be used to obtain a triple-layered laminate by coextrusion, for example, and the desired triple-layered porous film can be manufactured by immersing the laminate in isopropyl alcohol for 0.5 to 60 hours at 20 to 60°C.

[0046]

The laminated porous film of the present invention should have a mean porosity of between 30 and 65%, and preferably between 35 and 50%. "Porosity" means the values measured in the following manner.

[0047]

A sample (5 cm × 5 cm) is immersed for 6 hours in mineral oil (by Aldrich), the mineral oil on the surface layer is thoroughly wiped off, the weight (W2) is then obtained, and the pore volume (V1) is determined by the following equation from the weight of the sample (W1) prior to immersion and the mineral oil density (ρ).

$$V1 = (W2 - W1)/\rho$$

[0048]

The porosity (P) is calculated by the following equation from the apparent volume (value calculated from the thickness and dimensions) V2 and the pore volume V1.

$$P = V1/V2 \times 100 (\%)$$

[0049]

A mean porosity of less than 30% results in low nonaqueous electrolyte absorption and retention, which is unsuitable for electrochemical devices, whereas a porosity of more than 65% tends to result in a separator with inadequate mechanical strength.

[0050]

The laminated porous film should have a mean pore diameter of between 0.01 and 5 μm , and preferably between 0.1 and 0.5 μm . "Mean pore diameter" means the value determined by the half dry method using ethanol based on ASTM F-316-86 using a sample with a measuring area of 20 mm \varnothing .

[0051]

A mean particle diameter of less than 0.01 μm results in a separator with substantial electrical resistance, making it unsuitable for electrochemical devices, whereas a value of more than 5 μm results in a greater possibility of shorts caused by the penetration of carbon beads on the electrode surface.

[Use of Laminated Porous Film/Separator]

[0052] Electrochemical Devices

The laminated porous film in the present invention is used as an electrode separator in electrochemical devices.

[0053]

The "electrochemical device" referred to here means battery cells, particularly lithium cells and lithium ion cells, electrolytic capacitors, and any other device featuring the use of electrical energy or its storage, or other electrochemical phenomena.

[0054]

Typical examples include lithium cells and, more broadly, nonaqueous electrolyte cells. Such cells are composed of: a negative electrode with an active material consisting of a light metal such as lithium or sodium; a positive electrode with an active material consisting of a metal compound having oxidation powder such as manganese dioxide; a separator interposed between the negative and positive electrodes; and a nonaqueous electrolyte such as one obtained by dissolving an electrolyte such as lithium perchlorate in a nonaqueous solvent such as a solvent mixture of propylene carbonate and 1,2-dimethoxyethane. The details and specific structure of such cells are well known. One may refer, for example, to *Koseino Denchi no Zaishin Gijutsu Manyuaru [Manual on Latest Techniques for High Performance Cells]* (published by Sogo Gijutsu Center). The electrode assembly in such cells is typically obtained by rolling up a composite sheet consisting of a separator impregnated with a nonaqueous electrolyte between the positive and negative electrode sheets.

[Working Examples]

[0055] Working Example 1

For the layer B resin, 100 phr DOP was melt blended at 230°C with poly (butene-1) (tradename Buron, by Mitsui Petrochemical Industries; melting point: 123°C) using a twin screw extruder to make pellets. For the layer A resin, 65 phr DOP was similarly melt blended at 260°C with poly (4-methylpentene-1) (tradename TPX, by Mitsui Petrochemical Industries; melting point: 235°C) to make pellets.

[0056]

The resulting pellets were melt extruded at 240°C from three extruders with 370 mm wide triple-layered coextrusion T dies to form molten sheets consisting of A/B/A layers, which were cooled on a 60°C chill roll to obtain porous film starting material. The starting material was cut into 200 mm squares, which were ultrasonically treated for 5 minutes in 30°C isopropyl alcohol. The sheets were dried, uniaxially drawn 1.5-fold at room temperature, and then heat treated for 30 minutes at 60°C to obtain laminated porous film. Examination of the cross section of the resulting laminated porous film by polarizing microscope revealed that the A/B/A layers were 7, 12, and 7 μm thick, respectively. The mean porosity was 46%, and the mean pore diameter was 0.26 μm . The shut down properties of the resulting laminated porous film, assuming heat produced by shorts between the electrodes of the electrochemical device, were examined in the following manner.

[0057]

The resulting laminated porous film was impregnated with electrolyte (1 mol/L lithium perchlorate dissolved in 1:1 mixture of propylene carbonate and 1,2-dimethoxyethane), and it was then fixed between two 5 cm² platinum electrodes to fabricate a measuring cell. As the measuring cell was heated, AC current (1 KHz, 4 V) was applied between the electrodes of the measuring cell using an LCR meter (model 4274, by Yokogawa Hewlett Packard) to measure the changes in AC electrical resistance (Ω·cm²). The shut down temperature was the temperature showing electrical resistance 10,000 times the initial electrical resistance at room temperature. The shut down temperature of the laminated porous film was 124°C. The shut down state was maintained up to 230°C with subsequent heating, indicating good shut down properties and safety.

[0058] Working Example 2

For the layer B resin, 100 phr DOP was melt blended at 230°C with poly (butene-1) (tradename Buron, by Mitsui Petrochemical Industries; melting point: 123°C) using a twin screw extruder to make pellets. For the layer A resin, 65 phr DOP was similarly melt blended at 260°C with poly (4-methylpentene-1) (tradename TPX, by Mitsui Petrochemical Industries; melting point: 235°C) to make pellets. For a layer resin different from the above (referred to as layer A' resin), 70 phr DOP was similarly melt blended at 240°C with polypropylene (tradename Chisso Polypro, by Chisso Corporation). The resulting pellets were melt extruded at 240°C from three extruders with 370 mm wide triple-layered coextrusion T dies to form molten sheets consisting of A/B/A' layers, which were cooled on a 60°C chill roll to obtain porous film starting material. The starting material was cut into 200 mm squares, which were ultrasonically treated for 5 minutes in 30°C isopropyl alcohol. The sheets were dried, uniaxially drawn 1.5-fold at room temperature, and then heat treated for 30 minutes at 60°C to obtain laminated porous film. Examination of the cross section of the resulting laminated porous film by polarizing microscope revealed that the A/B/A' layers were 6, 5, and 8 µm thick, respectively. The mean porosity was 44%, and the mean pore diameter was 0.24 µm. The shut down properties of the resulting laminated porous film, assuming heat produced by shorts between the electrodes of the electrochemical device, were examined in the same manner as in Working Example 1. The shut down temperature of the laminated porous film was 124°C. The shut down state was maintained up to 230°C with subsequent heating, indicating good shut down properties and safety.

[0059]

[Effects of the Invention]

In the electrode separator consisting of polyolefin resin laminated porous films for use in electrochemical devices in the present invention, a low melting point layer is interposed between high melting point resin films. The thickness, and thus the volume, of the intermediate layer resin is sufficient to overcome the poor shut down function

during shorts characteristic of low melting point resin films which are in contact with the electrodes, as note in the Summary of the Invention section.